Crystal structure of copper(I) zinc indium disulfide, $(Cu_{1.02}Zn_{0.11})In_{0.87}S_2$

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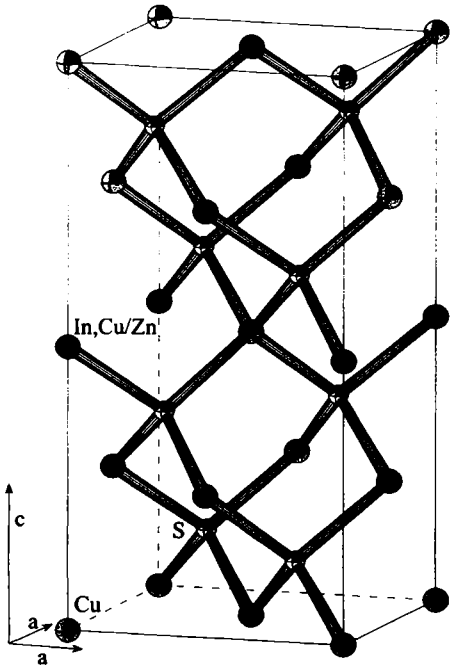

Abstract

$Cu_{1.02}In_{0.87}S_2Zn_{0.11}$, tetragonal, $I\bar{4}2d$ (No. 122), $a = 5.5397(5)$ Å, $c = 11.081(2)$ Å, $V = 340.1$ Å^3, $Z = 4$, $R_{gt}(F) = 0.028$, $wR_{ref}(F^2) = 0.065$, $T = 293$ K.

Source of material

Single crystals of composition $Cu_{1.018(8)}In_{0.906(8)}Zn_{0.112(4)}S_{1.96(1)}$ with size of 0.1 to 1 mm were obtained by exothermal chemical vapour transport starting with mixed crystal powder precursers (purity > 99.999%). The synthesis was performed in quartz ampoules (length 85 mm, internal diameter 13 mm) over 10 days using a temperature gradient between 1133 K and 1103 K. The transport medium was iodine (3 mg/ccm). The chemical composition of the crystal was determined by electron microprobe (CAMECA SX100, 15kV/20mA, standards: synthetic roquesite, $CuInS_2$, and sphalerite, ZnS).

Discussion

As reported [1] rotation twins (T111) are typical for thin films of corresponding materials. Microtwinning was detected for the investigated crystal by measuring reflections with systematic deviations from integral indices. The twin law is given by the matrix (–0.33 –0.67 –0.33 / –0.67 –0.33 0.33 / –1.33 1.33 –0.33). Furthermore the crystal contained orientation domains resulting in additional reflections being confirmed by transmission electron microscopy [2]. The orientation of the tetragonal domains is described by the matrices (0 1 0/0 0 –0.5/–2 0 0) and (0 0 0.5/1 0 0/0 2 0) leading to an overlap of reflections with partial merohedry. Therefore, it was possible to determine the contribution of each domain component by comparing the measured intensities. A twin refinement using the HKLF5 format and three batch scale factors (BASF) which were 0.304(2), 0.308(2) and 0.080(4) confirmed the assumed twin laws and the contribution intensity of each twin or domain component. The resulting chalcopyrite-type structure is very similar to the model found by Abrahams and Bernstein [3] showing a difference in the x-parameter of sulfur representing a smaller tetragonal distortion. Using the chemical composition of the material as constraint in the refinement the site occupancies were determined. The results show t : In-site being occupied with 85% In and 15% Zn and/or Cu. B : cause a differentiation of Cu and Zn is not possible by using X-r : data, further neutron diffraction measurements are planed.

Table 1. Data collection and handling.

Crystal:	black tetrahedron, size 0.11 × 0.18 × 0.18 mm
Wavelength:	Mo K_α radiation (0.70932 Å)
μ:	139.5 cm^{-1}
Diffractometer, scan mode:	Bruker AXS P4, ω
$2\theta_{max}$:	100.42°
$N(hkl)_{measured}$, $N(hkl)_{unique}$:	1502, 1502
Criterion for I_{obs}, $N(hkl)_{gt}$:	$I_{obs} > 2\,\sigma(I_{obs})$, 1191
$N(param)_{refined}$:	15
Program:	SHELXL-97 [4]

Table 2. Atomic coordinates and displacement parameters (in Å^2).

Atom	Site	x	y	z	U_{11}	U_{22}	U_{33}	U_{12}	U_{13}	U_{23}
M(1) [a]	4a	0	0	0	0.0236(7)	U_{11}	0.022(1)	0	0	
M(2) [b]	4b	0	0	1/2	0.0150(3)	U_{11}	0.0144(7)	0	0	0
S	8d	0.2313(1)	1/4	1/8	0.0136(4)	0.0142(5)	0.0119(7)	0	0	0.0001(

a: M(1) = 0.98(2)(Cu,Zn) + 0.02In
b: M(2) = 0.15(2)(Cu,Zn) + 0.85In

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